



Slurry-based chemical hydrogen storage systems for automotive fuel cell applications



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HIGHLIGHTS

- Chemical hydrogen storage materials provide high hydrogen storage densities.
- Alane and ammonia borane represent endothermic and exothermic slurries.
- The system developed met most of the 2017 DOE technical targets for vehicles.
- Reduction of slurry mass is required to meet gravimetric density targets.
- Materials with higher storage capacity or solids loading are required.

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ABSTRACT

In this paper, the system designs for hydrogen storage using chemical hydrogen materials in an 80-kWe fuel cell, light-duty vehicle are described. Ammonia borane and alane are used for these designs to represent the general classes of exothermic and endothermic materials. The designs are then compared to the USDRIVE/DOE-developed set of system-level targets for onboard storage. While most DOE targets are predicted to be achieved based on the modeling, the system gravimetric and volumetric densities were more challenging and became the focus of this work. The resulting system evaluation determined that the slurry accounts for the majority of the system mass. Only modest reductions in the system mass can be expected with improvements in the balance-of-plant components. Most of the gravimetric improvements will require developing materials with higher inherent storage capacity or by increasing the solids loading of the chemical hydrogen storage material in the slurry.

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1. Introduction

Commercializing an integrated fuel cell power system for automotive applications is a topic that has continued interest because of the potential political and environmental benefits. The political benefits of such a system include the need to remove or relax the nation's dependence on foreign oil. Hydrogen for a fuel cell can be generated using non-petroleum processes. The

environmental benefits include reduction in vehicle emissions such as pollutants and greenhouse gases—the only byproduct being water. Hydrogen fuel cells also offer unprecedented vehicle efficiencies of up to 60% [1].

One of the shortcomings of fuel cells is the low gravimetric and volumetric densities of the hydrogen fuel. Gaseous hydrogen must be stored at low temperature (≈ 80 K) and/or high pressure (> 350 bar) to provide acceptable driving ranges in automobiles. Liquid hydrogen offers increased volumetric capacities but requires storage temperatures around 20 K [2]. In both cases, dormancy and safety issues are the critical challenges in storing neat hydrogen for automotive applications.

In an attempt to remove the limits imposed by the gravimetric and volumetric storage capacities of neat hydrogen, the U.S. Department of Energy's (DOE) Fuel Cell Technologies Office has funded the Hydrogen Storage Engineering Center of Excellence

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(HSECoE). The HSECoE is a team of universities, industrial corporations, and federal laboratories with the mandate to develop lower-pressure, materials-based, hydrogen storage systems for hydrogen fuel cell light-duty vehicles [3]. HSECoE is not engaged in development of new hydrogen storage materials themselves; rather, as an engineering center, it addresses engineering system design challenges associated with the currently available hydrogen storage materials. Three material-based approaches to hydrogen storage are being researched: 1) adsorbents, 2) metal hydrides, and 3) chemical hydrogen storage materials.

USDRIVE/DOE have established storage system targets to ensure that light-duty vehicles using these technologies have driving ranges comparable to today's vehicles while meeting commercial performance, cost, and reliability requirements [4]. On the basis of the promising hydrogen storage capacity, HSECoE has chosen chemical hydrogen storage materials for study. Chemical hydrogen storage materials are defined as those hydrogen-bearing materials that release hydrogen by breaking chemical bonds. Once these chemicals have been reacted to produce hydrogen, the material must be removed from the system and regenerated before it can be reused. This differs from other hydrogen storage materials that can be regenerated with hydrogen directly onboard the vehicle.

Several different storage materials have been evaluated, a fluid-based system was found to be the easiest means of material conveyance. Because many of the chemical hydrogen storage materials are solids, a means of creating a fluid-based system requires blending a finely powdered chemical hydrogen storage material with an acceptable liquid carrier agent to produce slurry. Although slurries can be challenging to handle, they can be transported on and off the vehicle using a flow-through process. Our focus is the development of an automotive hydrogen storage system using a slurry-phase chemical hydrogen storage media.

2. Methods

The DOE has established system-level targets for onboard hydrogen storage systems for light-duty vehicles as shown in Table 1 [4]. The 2017 system-level targets were used as the basis of these system designs. The system designs assumed a fuel cell rated at 80 kWe and a net-usable hydrogen storage mass of 5.6 kg.

The technical targets provide boundaries for the system size (system gravimetric and volumetric targets), system performance (startup, transients, drive cycles and efficiency), filling conditions, operating conditions (acceptable ambient temperature range), durability (cycle life), safety, and hydrogen quality (purity, temperature, and pressure limitations). The slurry-based chemical hydrogen storage system was designed to meet all of these targets. Although no system cost target was provided, cost minimization efforts (e.g., materials of construction, component selection, etc.) also were undertaken during the system design phase.

The slurry-phase system design was based on the results of small-scale testing with low concentration slurries. The tests provided the basic kinetics that was used to estimate reactor performance. In addition to measuring reaction kinetics, thermodynamic parameters (e.g., heat of reaction and heat capacity), hydrogen impurities, and rheological properties for both hydrogenated and dehydrogenated fuel were measured [5,6]. System component validation was accomplished using either the actual storage materials or simulants.

The initial design was based on using ammonia borane (AB) as the chemical hydrogen material. It was selected because of its promising net-usable hydrogen storage capacity of approximately 16 wt% neat, based on an experimentally derived value of 2.5 equivalents hydrogen generated per mole of AB [7]. Ammonia borane is a white waxy material with good thermal stability (shelf life of weeks at temperature less than 60 °C) [7]. It can be handled

Table 1
DOE technical targets for onboard hydrogen storage systems for light-duty vehicles [1].

Storage parameter	Units	2010	2017	Ultimate
System gravimetric capacity: usable, specific-energy from H ₂ (net useful energy/max system mass)	kWh kg (kg H ₂ /kg system)	1.5 (0.045)	1.8 (0.055)	2.5 (0.075)
System volumetric capacity: usable, specific-energy from H ₂ (net useful energy/max system volume)	kWh L (kg H ₂ /L system)	0.9 (0.028)	1.3 (0.040)	2.3 (0.070)
Storage system cost	\$/kWh net	TBD	TBD	TBD
• Fuel cost	(\$/kg H ₂)	(TBD)	(TBD)	(TBD)
	\$/gge at pump	3–7	2–4	2–4
Durability/operability:				
• Operating ambient temperature	°C	–30/50 (sun)	–40/50 (sun)	40/50 (sun)
• Min/max delivery temperature	°C	–40/85	–40/85	–40/85
• Operational cycle life (1/4 tank to full)	Cycles	1000	1500	1500
• Min delivery pressure from storage system: FC-fuel cell, ICE-internal combustion engine	Bar (abs)	5 FC/35 ICE	5 FC/35 ICE	5 FC/35 ICE
• Max delivery pressure from storage system	Bar (abs)	12 FC/100 ICE	12 FC/100 ICE	12 FC/100 ICE
• Onboard efficiency	%	90	90	90
• “Well” to powerplant efficiency	%	60	60	60
Charging/discharging rates:				
• System fill time (5 kg)	min (kg H ₂ /min)	4.2 (1.2)	3.3 (1.5)	2.5 (2.0)
• Minimum full flow rate	(g s ^{–1})/kW	0.02	0.02	0.02
• Start time to full flow (20 °C)	s	5	5	5
• Start time to full flow (–20 °C)	s	15	15	15
• Transient response 10%–90% and 90%–0%	s	0.75	0.75	0.75
Fuel Purity (H ₂ from storage)	% H ₂	SAE J2719 and ISO/PDTS 14687-2 (99.97% dry basis)		
Environmental health & safety:				
• Permeation & leakage	Scc/h	Meets or exceed applicable standards		
• Toxicity	—			
• Safety	—			
• Loss of usable H ₂	(g h ^{–1})/kg H ₂ stored	0.1	0.05	0.05

Useful constants: 0.2778 kWh MJ; 33.3 kWh hg H₂; 1 kg H₂ ≈ 1 gal gasoline equivalent.

around air and water at room temperature, but dust formation should be avoided [8]. However, AB is not without challenges. The low specific gravity of neat AB (0.74 kg L^{-1}) poses technical challenges in slurry preparation because of phase separation [9]. In contrast, the specific gravity of dehydrogenated AB is 1.64 kg L^{-1} —over twice as dense as neat AB. In both cases, the densities of hydrogenated and dehydrogenated AB produce stratified heterogeneous mixtures. Consequently, these mixtures require mixing of both the feed and product materials during storage. The exothermic dehydrogenation of AB ($-21.7 \text{ kJ (mol H}_2\text{)}^{-1}$) poses challenges with the carrier fluid (e.g., flash vaporization, chemical side reactions, etc.) [10]. Ammonia borane also poses challenges because, upon dehydrogenation, the products tend to form a pseudo-gelatinous matrix that causes reactor fouling. Reactor fouling can be mitigated by actively mixing the slurry during dehydrogenation, thus preventing agglomeration. Last, AB generates fuel cell impurities (i.e., ammonia, borazine, diborane, etc.) that require removal prior to reaching the fuel cell [11].

With minor modifications to the exothermic system design (e.g., slurry-based AB), the system design can be recast for use with endothermic materials (e.g., slurry-based alane). Neat alane is a crystalline powder that has a net-usable hydrogen storage capacity of 10 wt% [12]. It has good thermal stability but is reactive with water and air. It has a specific gravity of 1.49 kg L^{-1} before reaction and reacts to produce aluminum metal (S.G. = 2.7 kg L^{-1}). The high densities once again result in the need for mixing the feed and product prior to movement. Because alane dehydrogenation is endothermic (11.4 kJ mol^{-1}), parasitic heat loads are required to drive the reaction [12]. In contrast to AB, the hydrogen selectivity for alane dehydrogenation has been observed to be unity, thus offering a reduction or elimination of hydrogen purification components.

The system mass for both alane and AB system designs were determined to be the most challenging technical target to meet. As a result, our system design efforts focused on minimizing the system mass rather than volume. The largest fraction of the overall system mass is the hydrogen storage slurry material itself, which accounts for over 50% of the system mass. Given the large mass percentage attributed to the media, research efforts were performed to maximize the solids loading while maintaining slurry viscosities less than 1500 cP. Several different carrier liquids, additives, and synthesis methods were evaluated to increase the solids loading (i.e., net-usable hydrogen storage capacity) [6]. For the purposes of system design and performance evaluations, a 50 wt% slurry was used (Table 2). Triton X-15, a DOW chemical surfactant, was added to the slurry to improve its stability and to prevent foaming.

The system design used commercially available components where possible, taking into account the temperature, pressure, and material compatibility. *A priori* estimates of mass, volume, and cost were used for components that were not commercially available. We anticipated that the cost and size of the off-the-shelf components would be reduced as they were developed and mass-produced for the automotive industry.

System performance and viability assessments were performed using models developed in Simulink® [13]. The primary inputs to

the system model were the simulated drive cycles, system design parameters, and material properties. The system model outputs were system-operating parameters such as flow rates, temperatures, and pressures predicted during the drive cycle of interest. The HSECoE has selected four simulated drive cycles to assess the transient behavior of the chemical hydrogen storage system design. The simulated drive cycles include 1) a highway cycle [UDDS + HWFET], 2) an aggressive driving cycle [US06], 3) a cold-start cycle [cold FTP], and 4) a hot cycle [SC03-Hot]. The aggressive US06 drive cycle uses a maximum 80 kW_e hydrogen demand ($1.6 \text{ g H}_2 \text{ s}^{-1}$). The cold FTP and hot SC03 have ambient operating temperatures of -20 and 35°C , respectively [14,15].

System component sizing was adjusted to ensure that these drive cycles could be met but not exceeded. The system design was not oversized beyond the minimum required in an effort to meet the system gravimetric targets. Where possible, multiple components were consolidated into one to minimize the system mass. As the system design was developed, components were added and removed to reduce complexity where possible while maintaining functionality. For example, as an automotive rather than a research application, only instrumentation actually required for operation is included. The designs presented here are still only preliminary. Experimental validation of most of the key components is required, and the design must be updated based on the validation results.

3. System design

The current exothermic system design is shown in Fig. 1. The system design was developed to be flexible and adaptable to a wide range of fluid-phase chemical hydrogen storage materials. Refinement of the system design and system model will continue as additional testing is performed. The system operation and the basis for its selection are described in this section.

The hydrogenated slurry/fuel is loaded on the vehicle where it is stored in a volume-displacement tank (TNK-1). The volume-displacement tank consists of a membrane separating the feed side of the tank from the product side. As fresh slurry is loaded into the tank, the membrane displaces spent slurry out of the tank and back to the filling/transfer station for reprocessing. During system operation when hydrogen is being generated, the fresh slurry is transported out of the feed side of the tank through the process and then back into the spent slurry side of the volume-displacement tank. The advantage of using a volume-displacement tank is that the overall tank volume is reduced by a factor of two. The volume-displacement tank is not under pressure ($\sim 1 \text{ atm}$) nor will it experience high temperatures ($<60^\circ \text{C}$). As a result, it can be a conformable tank made of lightweight, polymeric materials.

Stratified, heterogeneous slurries result from density differences in the solids and the liquid carrier matrix. Stratification occurs when the solid-phase density is less than the carrier matrix, causing the solids to float or, when the solid-phase density is greater than the carrier matrix, causing the solids to settle. In both cases, stratification is undesirable so active mixing is required. Testing was performed to identify approaches that would homogenize the slurry with minimum equipment and effort while not impacting the tank design. The preferred alternative found was the “press-pot” approach. The press-pot is a perforated plate nearly the size and shape of the tank that is cycled up and down to produce a homogenous mixture. These plates create vortices that quickly mix the stratified solids (Fig. 2). Magnetically coupling the perforated plate with linear actuators on the outside of the tank may eliminate unnecessary feed-through connections.

Ammonia borane dehydrogenation requires elevated reaction onset temperatures. Rather than heat the system quickly to meet the stringent startup time required by the DOE technical targets,

Table 2
Properties of a 50 wt% ammonia borane slurry in AR-20 silicone oil.

Property	Value	Units
Hydrogen capacity	7.6	wt%
Plastic viscosity	600	cP
Undisturbed yield stress	130	Pa
Triton X-15 concentration	1	wt%
AB particle size	<500	microns

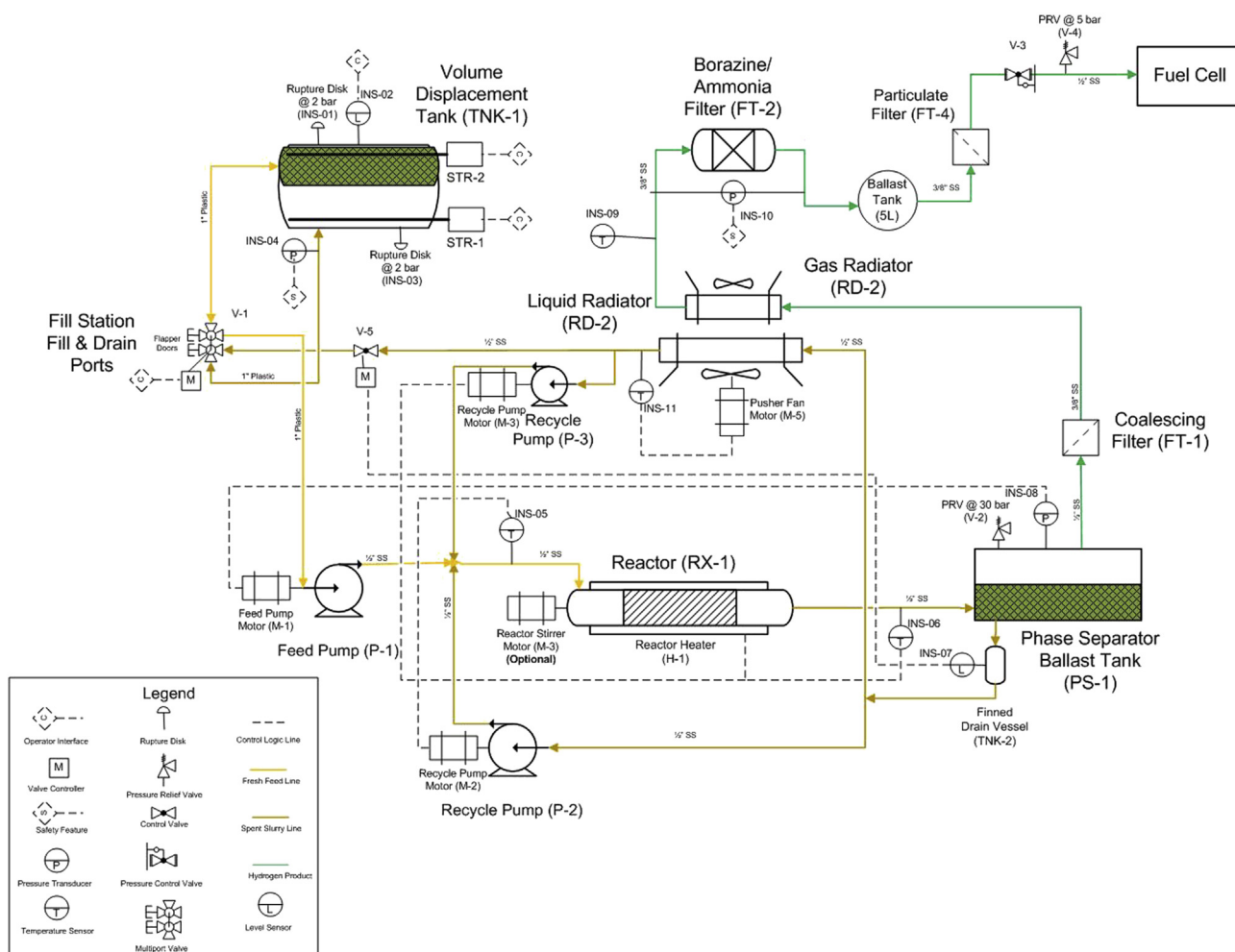


Fig. 1. System process flow diagram for an exothermic chemical storage material.

hydrogen gas is stored in a ballast tank. The ballast tank allows hydrogen to immediately flow to the fuel cell during cold startup while the storage system is warming to the required temperature to initiate the thermolysis reaction. A hydrogen ballast tank with an estimated volume of 30 L and pressurized to 25 bar can store enough hydrogen for the most aggressive drive cycles during the first few minutes of system heating. The ballast tank also provides hydrogen to accommodate the transients associated with the drive

cycles described above. As a result, for a short duration, higher hydrogen flow rates are available to the fuel cell than can be provided by a storage system. By having a ballast tank, the system is not required to produce the full 80 kW_e. In fact, even with the most aggressive US06 drive cycle that has shown requests for 80 kW_e, the maximum hydrogen output for the system is slightly over 20 kW_e.

The reactor is a modified plug-flow design. The dehydrogenation reaction is assumed to be a non-catalytic thermolysis. Small-scale, flow-through reactor experiments have shown that active mixing is required to prevent reactor fouling. The reactor design includes axial mixing elements that provide active mixing for the entire reactor volume. In addition, axial mixing also promotes gas–liquid separation, thus mitigating reactor slugging. The reactor is heated on the outer surface with electrical resistance heaters to bring it to temperature and initiate the reaction. Although alternative, possibly more efficient heat sources were considered for providing heat to the reactor, the AB efficiency is already high, and electrical resistance heaters are the lightest weight alternative.

During startup, the heater surrounding the reactor is turned on to raise the temperature of the reactants to the light-off temperature. The fresh feed in the volume-displacement tank is homogenized before feeding into the reactor. Upon reaching the required light-off temperature (~3 min), the feed pump begins to move fresh feed into the reactor. Hot product at ~250 °C is re-circulated to mix with the feed. The recycle stream preheats the feed to



Fig. 2. Validation Test of the “press pot” for active mixing in the volume-displacement tank using simulated slurry composed of polyethylene powder in silicone oil at 50 wt%.



Fig. 3. (a) Internal design of the Eaton filtration phase separator and (b) Energy transfer MDE finned tube slurry/gas radiator design.

eliminate the need to heat the reactor once the reaction is initiated. The recycle also increases the heat capacity of the slurry, diluting the feed and reducing the high temperatures associated with exothermic reaction heat. To maintain the reactor exit temperature at $<250^{\circ}\text{C}$ to prevent volatilizing the slurry fluidizing agent, producing high levels of impurities, or damaging the reactor and downstream components, the recycle can also include a fraction of cold spent slurry exiting the radiator.

Hydrogen is separated from the three-phase mixture in a phase separator developed by Eaton Filtration design group and UTRC. The two-stage design comprises a coalescing demister pad (first stage) and the Cempellar™ centrifugal separator (second stage). Hydrogen separation is performed using three principles: 1) gravity

separation similar to a knock-out pot, 2) impingement on a surface, and 3) the centrifugal flow generated as some of the three-phase mixture passes through the centrifugal separator (Fig. 3a). No slurry materials can be in the hydrogen, and no hydrogen can be in the remaining slurry. As a result, the separation requirements for the phase separator must be nearly perfect. The gas passes through a coalescing filter to remove any aerosol droplets. The hydrogen gas then passes through a radiator to lower its temperature to that required for the fuel cell feed. The radiator uses a finned tube configuration based on $\frac{3}{4}$ " OD aluminum fins and a $\frac{1}{4}$ " stainless-steel tube from Energy Transfer MDE (Fig. 3b). Improvements in heat transfer were accomplished by inserting a turbulator™ inside the radiator tube. A turbulator™ is a twisted tape that creates

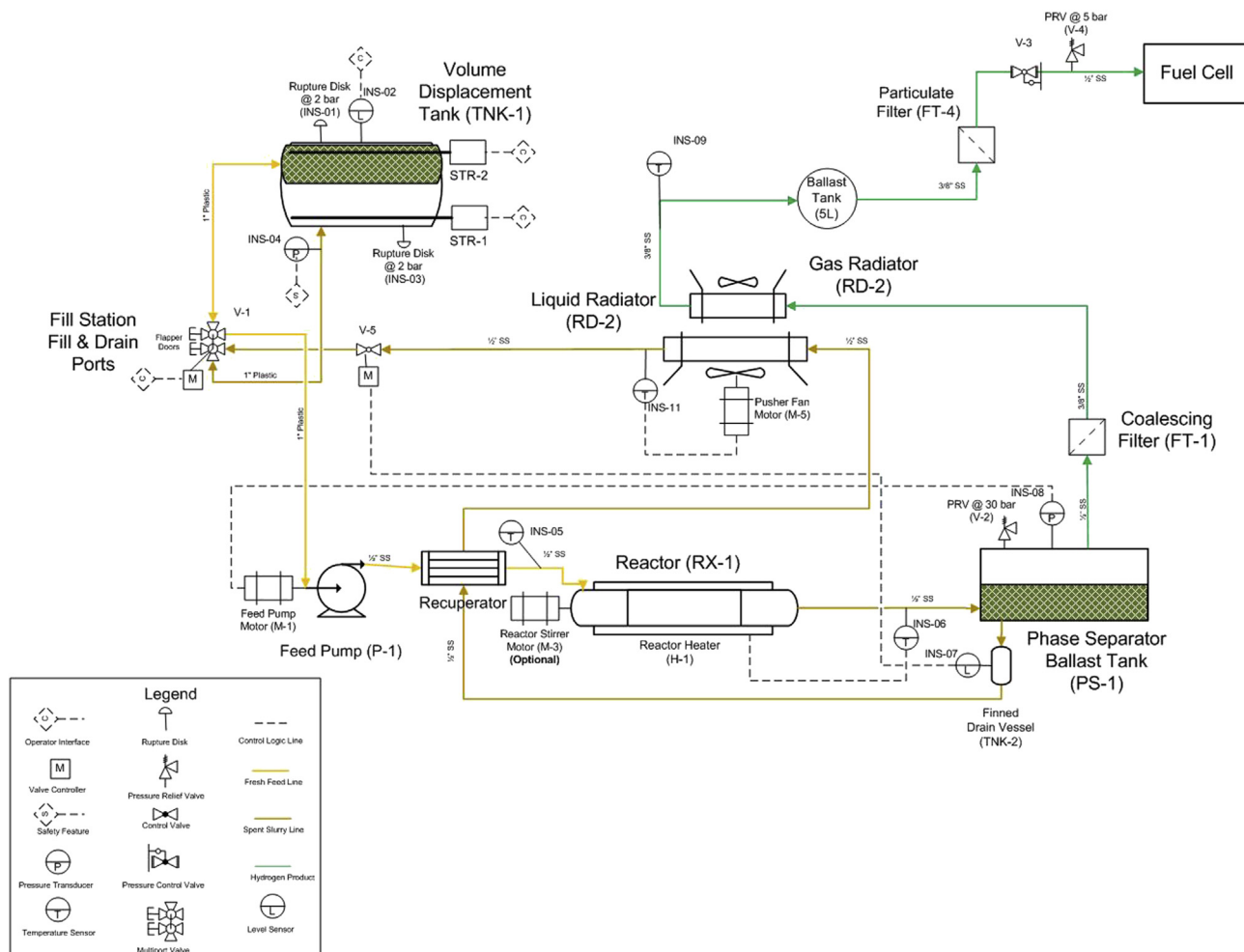


Fig. 4. System process flow diagram for an endothermic chemical storage material.

turbulence in the radiator and increases the heat transfer coefficient between the hydrogen and the tube wall. Increasing the heat transfer coefficient correlates to decreased radiator volumes and masses.

Fuel cell impurities generated from chemical hydrogen storage media require removal prior to reaching the fuel cell. The hydrogen delivered to the fuel cell must be greater than or equal to 99.97% (Table 1). The SAE J2719 hydrogen quality guidelines for fuel cell vehicles list a number of impurities and there maximum concentration. Dehydrogenation of AB is known to produce fuel cell impurities; namely, ammonia, borazine, and diborane. Doped activated carbon adsorbent beds were demonstrated to adsorb these impurities and produce fuel cell grade hydrogen [16,17]. Based on our system design, the size of these adsorbent beds is based on the amount of impurities anticipated and an 1800 mi replacement frequency. The fuel cell grade hydrogen ($T = 80^\circ\text{C}$ and 25 bar) is then fed to the fuel cell at 5 bar (Table 1) via a pressure regulator.

The slurry from the phase separator enters a collection vessel where the hydrogen gas in the slurry can coalesce and gravity separate from the condensed phase. This additional separation is required based on the experimentally observed foam that has been produced in the validation studies with United Technologies Research Center. Once this final separation is complete, a fraction of the slurry is recycled back to the reactor and the remaining hot material passes through the slurry radiator with 1-in. outer-diameter aluminum fins and a $3/8$ -in. stainless-steel tube. The slurry radiator has a similar design to the gas radiator, using finned tubes and a turbulatorTM. The radiator lowers the slurry temperature to a safe handling temperature of less than 60°C , thus eliminating the premature, uncontrolled hydrogen release from the fresh fuel located in the adjacent storage volume. A valve controls the flow of the cooled slurry returning to the volume-displacement tank to maintain a constant overall system pressure near the set point of 25 bar. Because the volume-displacement tank has a limited volume and is maintained at atmospheric pressure, we assumed that any hydrogen remaining in the slurry as it returns to the volume-displacement tank would be vented to the atmosphere.

All slurry piping is designed with tubing of at least $1/2$ -in. diameter to prevent plugging. The high-pressure hydrogen gas lines were sized to $3/8$ -in. diameter. The system is instrumented as required with thermocouples, pressure transducers, and level gauges to provide adequate system control.

The system design described above and provided in Fig. 1 is for an exothermic reaction such as AB dehydrogenation. For a mildly endothermic reaction (e.g., alane dehydrogenation), the system design is modified slightly (see Fig. 4). For the endothermic system design, the recycle stream is replaced with a recuperator that allows heat transfer from the product to the feed without diluting the feed stream with spent product, thus, minimizing unnecessary heating requirements. Its design is a $1/2$ -in. tube within a $3/4$ -in. tube, and flow is countercurrent. The reactor heater for endothermic materials operates during startup (as is the case of an exothermic reaction) and continuously during reactor operation. One additional change in the system design is that the adsorbent beds employed to remove fuel cell impurities have been eliminated because alane does not produce fuel cell impurities during dehydrogenation.

The original design is based on the properties of AR-20 (Polyphenyl-methylsiloxane from Sigma–Aldrich). While this oil was reasonably good for preliminary validation testing, there is a need for improved slurrying agents with even lower vapor pressures to minimize the need to remove them in the onboard hydrogen purification process. Oils such as those used for diffusion pumps are good candidates. Silicone oils like pentaphenyl trimethyl

Table 3

Dimensions and masses of the ammonia borane and alane systems.

System component	Size for AB system			Size for alane system		
	Mass (kg)	Volume (L)	Length (m)	Mass (kg)	Volume (L)	Length (m)
Slurry for 5.6 kg H ₂	75	83	—	127	102	—
Reactor (O.D. = 0.044 m)	0.9	0.8	0.5	1.9	1.5	1
Ballast tank	4.1	24	—	4.7	27	—
Impurities adsorbents	7.1	6.4	—	N/A	N/A	N/A
Gas radiator (I.D. = 0.005 m/ O.D. = 0.019 m)	0.2	0.1	0.7	0.1	0.1	0.4
Liquid radiator (I.D. = 0.008 m/ O.D. = 0.025 m)	0.7	1.1	1.25	0.5	0.9	1
Recuperator (I.D. = 0.011 m/ O.D. = 0.019 m)	N/A	N/A	N/A	0.3	0.2	0.5
Balance of plant	30.8	20.9	—	27.8	19.5	—

trisiloxane have a very high temperature stability and very low vapor pressure, both of which are highly desired when trying to minimize onboard hydrogen purification requirements. Additional work is required in this area.

4. Results and discussion

Based on the properties of 50 wt% slurries of AB and alane in silicone oil, the components for the systems described above were sized to produce 5.6 kg of net-usable hydrogen. The size of the volume-displacement tank was calculated based on amount of usable hydrogen in the slurry, while Simulink modeling was used to calculate the sizes of the reactor, heat exchangers, and ballast tank. The Simulink model sized the reactor volume for complete conversion and sized the ballast tank to meet the drive cycles both during startup and transient operations (Table 3). The modeling effort determined that, with a ballast tank of 30 L for both AB and alane and reactor lengths of 0.5 m for AB and 1.0 m for alane, the hydrogen demands for all four drive cycles could be met. The hydrogen production estimates from the model relative to the hydrogen required for the most challenging US06 drive cycle are shown in Fig. 5.

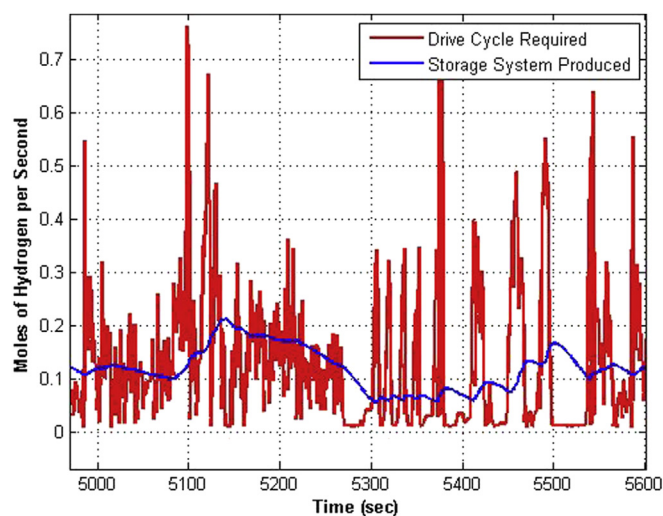


Fig. 5. Comparison of the vehicle hydrogen needs and the storage system production for the US06 drive cycle using 50 wt% ammonia borane slurry.

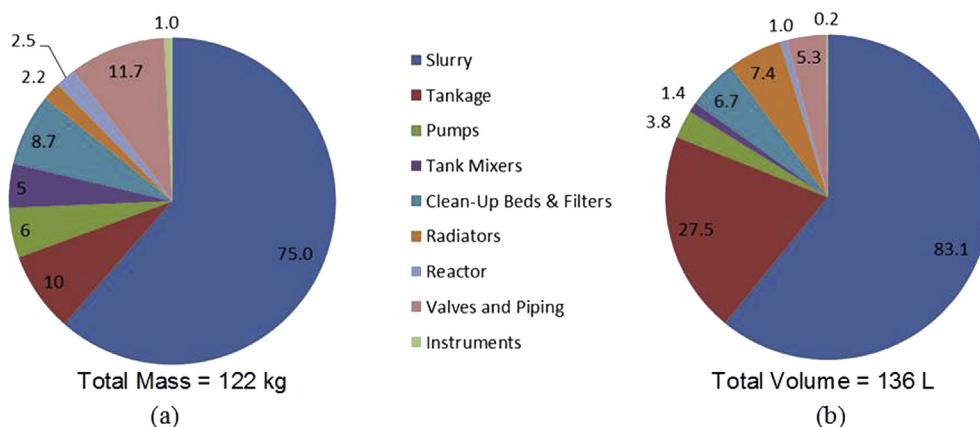


Fig. 6. (a) Mass (kg) and (b) Volume (L) distributions of system components for an ammonia borane hydrogen storage system.

Although there are peak hydrogen requirements beyond that produced by the storage system, the ballast tank provide sufficient excess hydrogen to address these needs. Similar results have been observed for both the AB and the alane system designs [13]. The size of the cleanup system was based on the anticipated levels of impurities and the estimated adsorption capacity of those impurities. Estimates suggest the need for 6.8 kg of borazine/diborane adsorbent (4000 ppm) in the off-gas and 1.6 kg of ammonia adsorbent with 500 ppm in the off-gas [18].

The DOE has a technical target onboard efficiency of greater than 90%. Onboard efficiency is defined as the ratio of the amount of hydrogen sent to the fuel cell to produce power to drive the vehicle as compared to the amount of hydrogen produced by the storage system. The hydrogen used to produce power for the heaters, motors, and fans is considered parasitic power and reduces the onboard efficiency. For exothermic dehydrogenation reactions, the largest contributor of parasitic power is startup. In the case of endothermic systems, parasitic power not only comes from startup but also from reactor heating during operation to maintain the

reactor temperature. The Simulink model was used to estimate this onboard efficiency. In the case of AB, this efficiency was well over the targeted 90% for all drive cycles. In the case of alane, the onboard efficiency ranged between 75 and 85%. As a result, it did not meet the DOE target even though the recuperator being used to recover heat from the reactor and warm the incoming stream.

The “loss of usable hydrogen,” “fuel purity,” and “fill time” technical targets are assumed to be met with both AB and alane storage materials. Both materials have little to no reaction at temperatures $<60^{\circ}\text{C}$ for weeks or more [7]. Scoping experiments at Los Alamos National Laboratory have indicated that the fuel purity can be achieved using a coalescing filter and appropriately sized adsorbent beds. Unlike other hydrogen storage materials, such as compressed or cryo-compressed hydrogen, metal hydrides, or adsorbents, heat removal or high pressures do not affect the filling requirement. The chemical hydrogen storage materials can be pumped into the volume-displacement tank at very low pressure. The flow rate is only limited by the size of the lines and the pump. As a result, it is assumed that the target fill time can be met.

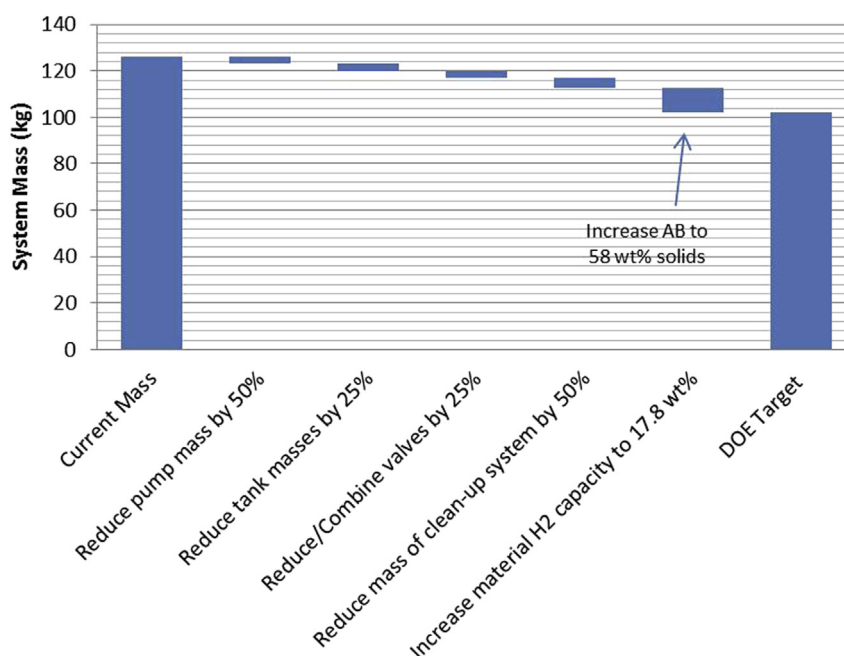


Fig. 7. Waterfall plot of one approach to achieving DOE targets with an ammonia borane-based storage system.

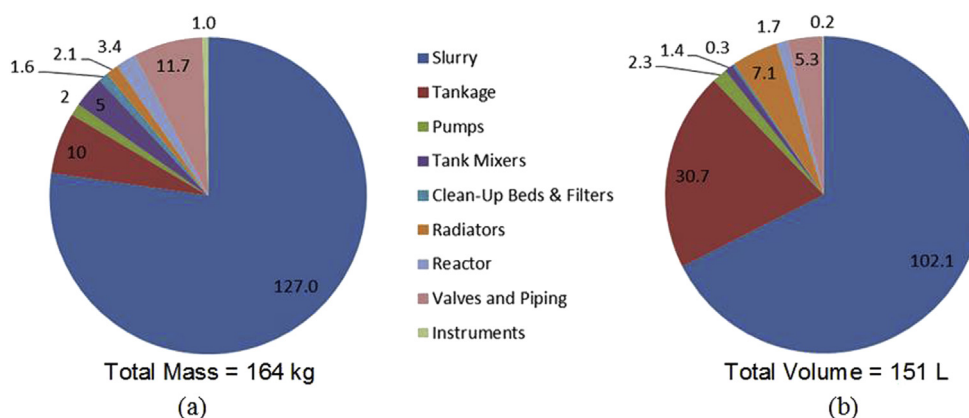


Fig. 8. (a) Mass (kg) and (b) Volume (L) distributions of system components for an alane-based hydrogen storage system.

The cost technical targets for the system have not been specified and the cost of the material is outside the scope of this work. As a result, these will not be included here. It should be noted however, that there are two costs for the chemical hydrogen storage material—the “first-fill” cost associated with the material's initial production and the “regeneration cost.” The “first-fill” cost of the storage material is much higher as it requires purchase of not only the hydrogen but also the other raw materials (i.e., aluminum in the case of alane and boron for AB). Once the material is produced, it will be regenerated repeatedly at a lower cost. The storage materials must at least meet the DOE technical targets for the regeneration cost to be considered.

The primary target that has been the focus of this work is the gravimetric capacity. Unlike most of the other targets that have been met by the design or are outside the scope of the system design, the system mass is a variable that system designers have worked to reduce. The system mass for AB was estimated to be 122 kg, and the volume was estimated to be 136 L. The distribution of weight and the volume for this system are shown in Fig. 6. Assuming 5.6 kg of usable hydrogen is produced, the total system

volume would be less than 140 L, thus meeting the 2017 DOE technical target for volume. In contrast, the mass is greater than the 102 kg maximum allowable to meet the technical target of 5.5 wt% hydrogen. Fig. 6 illustrates that the majority of the mass is in the slurry itself. Other large contributors are the tanks, hydrogen purification system components, valves, and piping. As part of this study, efforts were made to determine how the overall mass could be reasonably reduced to meet DOE targets. One possible pathway to reduce the system mass and meet the DOE gravimetric target is shown on the waterfall plot in Fig. 7. Although some mass reductions could come by using smaller components than can be found commercially or by combining two or more components into a single unit with multiple functions, these mass reductions are relatively minor. Similarly, a 25% reduction in the phase separator, volume-displacement, and ballast tanks achieves only modest improvements. Increasing the solids loading or the hydrogen content of the slurry would result in the most significant change.

An increase in the slurry hydrogen can be done by either increasing the current AB material from a solids concentration in the slurry from 50 to 58 wt% or by increasing the hydrogen content

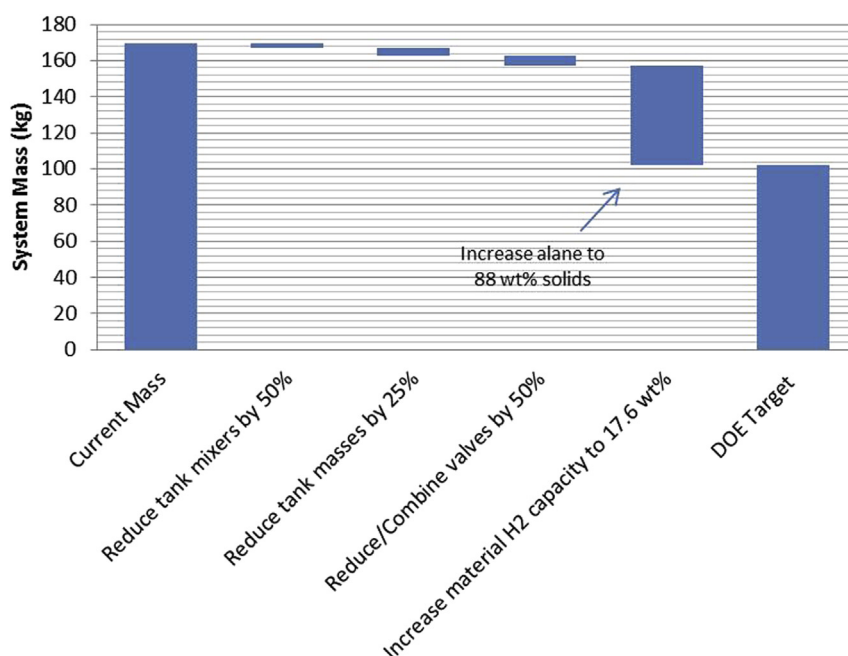


Fig. 9. Waterfall plot of one approach to achieving DOE technical targets with an alane-based storage system.

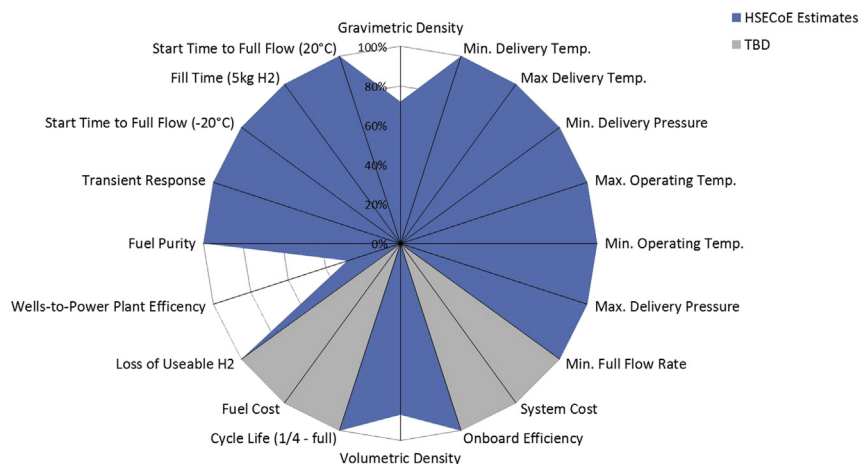


Fig. 10. Spider plot comparing DOE technical targets to AB system design.

of the storage material itself from 15.2 to 17.8 wt% with a 50 wt% loading. Both of these improvements would be a significant challenge because the AB slurry at 50 wt% is near the limit of its loading capacity [19]. Higher AB solids loadings tend to remain on top of the slurry rather than existing in a homogeneous mixture. Ammonia borane is a material with one of the highest hydrogen contents so identifying materials with higher concentrations will be challenging.

In the case of alane, the system is 42 kg heavier than the AB system and 162 kg heavier than allowed by the DOE gravimetric target. Furthermore, the system volume is 11 L over the DOE volumetric target. While no recycle pump or hydrogen purification components are required, the primary mass contributor results from the lower hydrogen loading of alane in a 50 wt% slurry as compared to that of AB: rather than being slightly over half of the total mass of the system, the alane slurry is almost three-quarters of the total system mass as shown in Fig. 8.

Using similar reduction factors for the size of the system balance-of-plant components, meeting the DOE targets would require increasing the solids loading from 50 wt%, which is its current basis, to 88 wt% (see Fig. 9). Alternatively, the hydrogen content of the solids has to be increased from its current value of 10 wt% to 17.6 wt% hydrogen with a 50 wt% solids loading of the slurry. As with AB, increasing either the solids loading of the alane or the hydrogen content of the chemical hydrogen storage material would be challenging.

Based on the current design, the best approach to meeting the DOE target for gravimetric density is to identify a material that is a liquid instead of a slurry, does not require an extensive cleanup system, and has fast kinetics at relatively low temperatures [19]. With this type of material, the size of the pumps, valves, and tubing could be further reduced; the cleanup system would be eliminated, and the ballast tank and reactor would be smaller. Despite these improvements, the most significant change would still be required—increasing the net-usable hydrogen content of the chemical hydrogen storage media. If the DOE mass target can be met, the DOE volumetric target also will be met.

5. Conclusion

The use of chemical hydrogen storage materials is a promising approach to providing a high-density medium for hydrogen storage for onboard vehicle applications. Systems have been developed that can meet most of the DOE technical targets for alane and AB as shown in the spider charts in Figs. 10 and 11, respectively. A summary of the two systems is shown in Table 4. Only the gravimetric and volumetric density and the well to power plant efficiency (WTPP) targets are not met with the current AB system.

The WTPP efficiency was calculated outside the scope of the HSECoE, but Strategic Analysis estimated it to be 19% for AB using hydrazine as demonstrated by Los Alamos National Laboratory [20,21]. The WTPP efficiency of alane also was low at 33%. Other

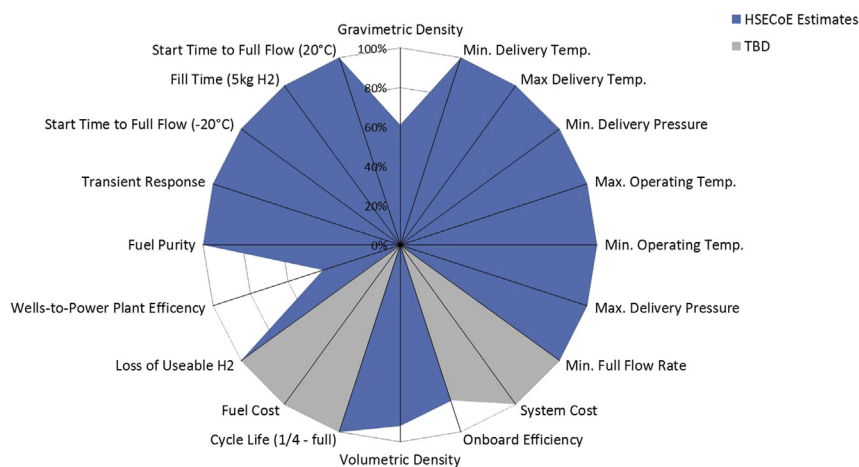


Fig. 11. Spider plot comparing DOE technical targets to an alane system.

Table 4

Comparison of ammonia borane and alane system designs.

System characteristic	50 wt% ammonia borane–silicone oil slurry	50 wt% alane–silicone oil slurry
Thermodynamics	Exothermic reaction	Endothermic reaction
Impurities generated	Borazine, ammonia, etc.	No impurities generated
Additional system equipment	Recycle pumps	Recuperator
Transient behavior	Meets drive cycles	Meets drive cycles
Onboard efficiency	>90% Onboard efficiency	<90% Onboard efficiency
Slurry concentration required to meet gravimetric targets	58 wt%	88 wt%

alternative approaches have not been explored, but achieving the required 60% WTPP efficiency will continue to be a challenge. In the case of alane, the onboard efficiency target also is less than the 90% target value. DOE technical targets have not been developed for the system and fuel costs. As a result, they cannot be presented on the spider charts, but work is underway to provide estimates of these costs [22].

6. Disclaimer

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